

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of:

Torsten Gottschalk-Gaudig et al.

Serial No.: 10/738,543

Filed: December 17, 2003

For: WATER-WETTABLE SILYLATED METAL OXIDES

Attorney Docket No.: WAS 0611 PUS

Group Art Unit: 1792

Examiner: Elena Tsoy Lightfoot

**APPEAL BRIEF UNDER 37 C.F.R. § 41.37**

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Commissioner for Patents  
U.S. Patent & Trademark Office  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

This is an Appeal Brief from the final rejection of claims 15 - 19 and 30- 36 of the Office Action mailed on December 10, 2008 for the above-identified patent application.

**I. REAL PARTY IN INTEREST**

The real party in interest is Wacker Chemie GmbH ("Assignee"), a corporation organized and existing under the laws of Germany, and having a place of business at Hanns-Seidel-Platz 4, München, Germany D-81737, as set forth in the assignment recorded in the U.S. Patent and Trademark Office on December 17, 2003 at Reel 014820/Frame 0784.

**II. RELATED APPEALS AND INTERFERENCES**

There are no appeals, interferences or judicial proceedings known to the Appellant, the Appellant's legal representative, or the Assignee which may be related to, directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

### **III. STATUS OF CLAIMS**

Claims 15 - 19 and 30 - 36 are pending in this application. Claims 15 - 19 and 30 - 36 have been rejected and are the subject of this appeal. Claims 1 - 14 and 20- 29 have been cancelled.

### **IV. STATUS OF AMENDMENTS**

An amendment after final rejection was filed on February 6, 2009, and has been accepted for entry.

### **V. SUMMARY OF CLAIMED SUBJECT MATTER**

Claim 15 claims partly hydrophobic silica particles (page 2, lines 4 - 5; page 3, line 5; page 5, lines 1 - 3) having a contact angle in air for water of less than 180°, a degree of coverage  $\tau$  of the surface of the silica with silylating agent residues, based on the total silica particle surface area, of  $1\% < \tau < 50\%$ , a density of surface silanol groups SiOH ranging from 0.9 to 1.7 SiOH/nm<sup>2</sup> particle surface area, a carbon content of more than 0% and up to 2% by weight, and a methanol number less than 30 (page 12, lines 3 - 12), by silylating silica particles prepared under anhydrous conditions (page 3, line 9) with:

I) an organosilane of the formula



where n is 1, 2 or 3

or mixtures of these organosilanes,

$R^1$  being a monovalent, optionally halogenated hydrocarbon radical having 1 to 24 carbon atoms, being identical or different at each occurrence, and being saturated, aromatic, monounsaturated, or polyunsaturated,

X each independently being halogen,  
 a nitrogen radical,  $\text{OR}^2$ ,  $\text{OCOR}^2$ , or  
 $\text{O}(\text{CH}_2)_x\text{OR}^2$ ,

$\text{R}^2$  being hydrogen or a monovalent hydrocarbon radical having 1 to 12  
 carbon atoms, and

x being 1, 2 or 3;

or

II) an organosiloxane composed of units of the formula

$(\text{R}^1_3\text{SiO}_{1/2})$ , and/or

$(\text{R}^1_2\text{SiO}_{2/2})$ , and/or

$(\text{R}^1\text{SiO}_{3/2})$

where  $\text{R}^1$  is as defined above,

the number of these units in one organosiloxane being at least 2; and I and II  
 being used alone or in any desired mixtures in a total amount of from 0.015  
 mmol/g to 0.15 mmol/g per 100  $\text{m}^2/\text{g}$  of silica BET surface area.

(Claim 1 as filed, page 2, lines 1 to page 3, line 3).

The invention also relates, as claimed in claim 16, to a partly hydrophobic silica  
 as claimed in claim 15, where the silylating is performed with the organosiloxane compound II  
 (page 2, lines 17 - 23), and claim 18, where the silylation is perfumed with a silane (I) and an  
 organosiloxane (II). (Page 2, lines 17 - 23).

The invention further pertains to partly hydrophobic silicas prepared by silylating  
 with a silane of the formula (I) of claim 15, wherein, as in claim 19, the  $\text{R}^1$  groups of the silane  
 (I) are selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, hexadecyl,  
 octadecyl, phenyl, biphenyl, naphthyl, benzyl, ethylphenyl, tolyl, and xylyl radicals. (Page 5, line  
 25 to page 6, line 14).

The invention further relates to partly hydrophobic silicas of claim 15, as claimed in claim 33, wherein the silylating agent is methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, and hexamethyldisilazane (page 6, line 23 to page 7, line 9).

## **VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL**

A. Claims 17 - 19, and 32 - 36 stand rejected under 35 U.S.C. § 112 paragraphs 1 and 2.

B. Claims 15 - 19 and 30 - 36 have been rejected under 35 U.S.C. § 103(a) as unpatentable over Barthel et al. U.S. 5,686,054 ("*Barthel*").

C. Claims 15 - 19 and 30 - 36 have been rejected under 35 U.S.C. § 103(a) as unpatentable over Tojo et al. U.S. 5,278,204 ("*Tojo*").

## **VII. ARGUMENT**

### **Part I: THE NATURE OF THE INVENTION**

The subject invention is directed to specific partly hydrophobic silicas which have very surprisingly been found to be able to act as dispersants in the preparation of water-in-oil (W/O) and oil-in-water (O/W) dispersions, as well as for preparation of multiphasic dispersions such as oil-in-water-in oil (O/W/O) and water-in-oil-in-water (W/O/W) dispersions. See, *e.g.* page 18, lines 3 - 10 and Example 10 on page 25. The ability to form stable dispersions without the use of surfactants such as non-ionic polyoxyalkylene polyethers or anionic surfactants such as petroleum sulfonates or the like is particularly surprising, and highly useful, in particular in compositions where such conventional surfactants might prove disadvantageous. Examples are coatings, where the hydrophilic portion of conventional surfactants can render the coating

hydrophilic and therefore less water resistant, and cosmetics, where many surfactants are also skin irritants to all or some.

Appellants discovered that silicas which meet the requirements of claim 15 are able to perform as a dispersing agent. The partly hydrophobic silicas are silicas silylated with a silane (I), an organosiloxane (II), or a mixture of these, and the partly hydrophobic silica resulting from silylation must meet six different requirements:

- 1) a contact angle  $\theta$  in air for water of less than  $180^{\circ}\text{C}$ ;
- 2) a degree of coverage  $\tau$  of the silica surface, based on total surface area, of  $1\% < \tau < 50\%$ ;
- 3) a density of surface silanol groups of 0.9 to 1.7  $\text{SiOH}/\text{nm}^2$  (SiOH groups per square nanometer);
- 4) a carbon content greater than 0 and up to 2.0 weight percent;
- 5) a methanol number of less than 30; and
- 6) the silylating agents used to silylate the silica used in amounts of 0.015 mmol/g to 0.15 mmol/g per 100  $\text{m}^2/\text{g}$  of silica BET surface area.

## II. BACKGROUND TECHNOLOGY

Before proceeding further, it is important that the characteristics of pyrogenic silica, silica silylation, and the concept of methanol number, which will play prominently in the ensuing argument be discussed.

## II.a. Pyrogenic (Fumed) Silica

Pyrogenic silica (silica prepared under anhydrous conditions) is produced by burning a silica precursor in a very high temperature flame. Typically,  $\text{SiCl}_4$  is burned in a flame of  $\text{H}_2$  and  $\text{O}_2$ . The water produced by combustion hydrolyzes the  $\text{SiCl}_4$  to  $\text{SiO}_2$ :



In addition to  $\text{SiCl}_4$ , other silanes, even organosilanes can be used. Examples are  $\text{HSiCl}_3$ ,  $\text{CH}_3\text{SiCl}_3$ ,  $\text{HSiCl}_2 - \text{SiCl}_2\text{H}$ , and the like. In the high temperature of the flame, primary particles fuse together to produce chain-like aggregates or "secondary particles," which agglomerate to form ultimate particles. The silica thus produced generally has a very high BET surface area, almost always in the range of  $25\text{m}^2/\text{g}$  to  $400^+\text{m}^2/\text{g}$ . Surface areas in the range of  $100 - 300\text{m}^2/\text{g}$  are very common. The silica is composed of  $\text{SiO}_{4/2}$  tetrahedra, each oxygen being bonded to two silicon atoms. However, at the edges and surface of the particles, not all the oxygens are capable of bonding to two silicon atoms, for obvious steric reasons. These oxygen atoms, bonded to but one silicon, satisfy their valence requirements by bonding to hydrogen, thus producing surface silanol groups. These rather acidic hydrogens are generally present in concentrations of about  $1.9$  to  $2.5 \text{ SiOH}/\text{nm}^2$ , and are responsible for the fact that fumed silica, when dispersed in water, is relatively acidic, a pH of about 4 being quite common.

The surface silanol groups are responsible for the hydrophilic nature of fumed silica. This hydrophilic nature prevents the silica from being easily incorporated into hydrophobic compositions like rubber and most polymers, and is also responsible for complete water wettability of fumed silica: when added to water and gently agitated, all the silica disperses or sinks below the surface.

## **II.b. Silylated or "Hydrophobic" silica**

Rubber and other thermoplastics which have hydrophilic fumed silica incorporated therein often have physical property problems, in addition to the problems of dispersing the silica into the polymer in the first place, which can be quite difficult. Rubbers with such fillers, for example, tend to harden over time, a phenomenon known in the industry as "crepe hardening."

In order to alleviate the above problems, the art proposed to eliminate all or substantially all of the silica silanol groups which are responsible for these problems, by derivatizing them with hydrophobic organic groups. The resulting silica is highly hydrophobic. This is generally done by silylation with a reactive silane such as trimethylchlorosilane, trimethylmethoxysilane, or hexamethyldisilazane (see pages 6 - 7 of the specification for others), or by reaction with an organosiloxane. As a result, the majority of the silanol groups are replaced with  $\text{-O-Si(R)}_x$  groups which are non-polar groups. The silica, which is now highly hydrophobic, can be easily incorporated into hydrophobic polymers, and shows little or no tendency to crepe harden.

However, such hydrophobic silicas are not dispersible in water. When added to water, they predominately float on the surface, no matter how intensive the stirring. The relative hydrophobicity may be determined by several methods, a principle method being the methanol number. The methanol number is the percentage of methanol in a water/methanol mixture which is necessary in order that the hydrophobic silica be completely wetted (i.e. no silica floats on the surface; all is dispersed). Thus, if a hydrophobic silica requires 50% methanol in water before it is completely wettable, the silica has a methanol number of 50. Silicas with methanol numbers  $> 50$  are highly hydrophobic.



## **II.c. Silylation**

### **1. Silicas Are Different, Even When The Surface Area Is The Same**

The amount of silylating agent required to produce hydrophobic silica of any given methanol number varies widely. The amount of silylating agent required to make quartz sand hydrophobic is very small, for example, while the amount used to render colloidal silica of 300 m<sup>2</sup>/g surface area may be quite large. The various silicas have different surface areas, and hence a different total number of silanol groups. Moreover, fumed silica produced by different processes have different concentrations of surface silanol groups. For example, two 200 m<sup>2</sup>/g silicas produced in different burners, or perhaps from different precursors, or at different temperatures, or all of these can have considerably different amounts of silanol groups per square nanometer. Since their surface areas are the same, these silicas will have markedly different SiOH content per gram.

### **2. Different Silylating Agents Have Different Silanol-Reactive Capabilities**

The silylating agents also make a great difference in the number of residual silanol groups. For example, 1 mol of (CH<sub>3</sub>)<sub>3</sub>SiCl has the capability of reacting with only 1 mol of SiOH groups, assuming reaction to be 100% complete, while 1 mol CH<sub>3</sub>SiCl<sub>3</sub> has the capability of reacting with 3 moles of SiOH groups. Hexamethyldisilazane has the capability of reaction with two SiOH groups.

### **3. Different Silation Reaction Processes Produce Different Silicas, Even When All Else Is The Same.**

Finally, different silylating reagents react to different degrees. Some may react virtually quantitatively, while others may react much less. Some may be actually physically adsorbed, without removing silanol groups at all by reaction.



Thus, even with a given silylating agent and a given silica, the degree of silylation will be very dependent upon the reaction conditions. For example, as described in the *Gottschalk-Gaudig* Declaration (Evidence Appendix), *Barthel* (the Barthel patent) took two identical silicas and silylated with identical amounts (32 weight percent!) of the same silylating agent, dimethyldichlorosilane, but under different conditions. *Barthel's* inventive silica, using 32 weight percent silylating agent, had a carbon content of 3.0 weight percent, and no SiOH groups were any longer detectable, while the comparative example, using the same weight percent and type of silylating agent, but in a prior art process, had only 50% of the carbon content of the inventive example (1.5%) had detectable silanol groups and a methanol number of 40 as compared to a methanol number 55 of the inventive example.

All these facts are well known to the skilled artisan, and all have been discussed at length in the many responses in this application.

### **III. THE REJECTIONS**

#### **A. The Rejections of the Claims Under 35 U.S.C. § 112**

In the Response of February 6, 2009, amendments were made to claims 17, 19, 32, 33, 34, 35 and 36. In the Advisory Action of February 10, 2009, the Examiner did not mention any of these amendments, and stated that the amendment "is not deemed to place the application in condition for allowance for the reasons of record set forth in the Final Office Action mailed on December 10, 2008."

Appellants submit that these claims fully meet the requirements of 35 U.S.C. § 112 ¶¶ 1 and 2 as amended, and believe that maintenance of the rejection was in error. Reversal of this rejection, if it is still maintained, is respectfully solicited.

**B.     The Claims Are Patentable Over *Barthel***

*Barthel* is directed to a process for silylating silicas to produce silicas which are highly hydrophobic. At column 9, lines 10 - 12, *Barthel* states that:

In accordance with these characteristics, the silica according to the invention can be designated as completely apolar or highly apolar.

In column 8, the "characteristics" referred to in the passage above are described. Noteworthy are the requirements that:

No isolated surface silanol groups can be detected. . . by IR spectroscopy. Even after prolonged shaking, the silica has no water-wettable fractions. The silica exhibits a methanol number. . . of greater than or equal to 50, preferably greater than 65 and more preferably greater than 75.

*Barthel* discloses a unique process for silylation involving fine atomization of the silylating followed by heat treating at elevated temperature and purifying at elevated temperature in a fluidized bed under nitrogen flow to remove unreacted silylating agent, which is used in large excess so that complete reaction with surface silanol groups and thus their elimination can be achieved. In Example 1, for instance, only 60% of the silylating agent reacts. In the comparative example, where gaseous silylating agent and higher reaction and purifying temperatures are used, only 30% of the silylating agent reacted. Neither of these products, however, meet the claim requirement of a methanol number of less than 30, and *Barthel* teaches against using silicas with methanol numbers less than 50 (such as the *Barthel* comparative silica with a methanol number of 40).

The position of the Office appears to be that if the same type of silylating agent within the range disclosed by *Barthel* is used to silylate a silica of a specific surface area, the result must be the same. However, as clearly discussed previously, this is not the case. Silica of 200 m<sup>2</sup>/g surface area, for example, may be prepared by numerous variations of pyrogenic silica manufacture, and may have distinctly different surface silanol content. Also, the conditions of silylation may be different as well, as can be the silylating agent.

One skilled in the art recognizes that there is no direct relationship between the amount of silylating agent, the silica surface area, the methanol number, and the carbon content. One cannot, for example, create a mathematical relationship which would allow one to input three of those four variables (there are more) and calculate the remaining one.

The Office appears to be missing the fact that *Barthel* is only directed to highly, completely or virtually completely hydrophobicized silica having a methanol number of 50 or more, preferably more. Regardless of whether one could choose a type of silylating agent, an amount of silylating agent, the silylation conditions, the silica surface area, the silica preparation method, etc., to create a partly hydrophobic silica having the claimed methanol number of less than 30<sup>1</sup>, *Barthel* teaches not to do so, but to instead select the above variables such that a methanol number  $\geq 50$  is always achieved. *Barthel* teaches away from producing silica with methanol numbers  $< 50$ . Teaching away is strong evidence of non-obviousness. *W.L. Gore v. Garlock*, 220 USPQ 303 (Fed. Cir. 1983).

The examples set forth in the specification are summarized in the table on the next page. These are Examples 1-5. Also in the table are additional examples and comparative examples performed under the direction of Dr. Torsten Gottschalk-Gaudig, and a *Barthel* example and *Barthel* comparative example from the *Barthel* patent. The *Barthel* requirements

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<sup>1</sup>A requirement of the subject invention, not *Barthel*. *Barthel* mandates a methanol greater than 50, preferably considerably higher.

for his fully hydrophobicized silica and the claimed silica are also set forth in the table. In the table, the various silylating agents are as follows:

DMDCS	dimethyldichlorosilane
HMDS	hexamethyldisilazane
OH-PDMS	hydroxyl-terminated-polydimethylsiloxane
MTCS	methyltrichlorosilane
TMES	trimethylethoxysilane.

Both HMDS and TMES result in formation of  $(\text{CH}_3)_3\text{Si-O}$  groups on the silica surface by reaction with surface silanol groups, and thus the silicas produced using these two different silylating agents will be derivatized in the same manner.

The details of the additional examples/comparative examples are as follows. The details for Examples 1-5 may be found in the specification.

Example 6 (according to the invention)

At a temperature of 25°C and under  $\text{N}_2$  inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 200  $\text{m}^2/\text{g}$  (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK<sup>®</sup> N20 from Wacker-Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 2.56 g of a mixture of 0.56 g of  $\text{H}_2\text{O}$  and 2.0 of MeOH and 4.29g of dimethyldichlorosilane (2.56 g of the mixture contains 1.60 g of DMDCS). The silica thus loaded is reacted at 250°C in a 100 L drying cabinet under  $\text{N}_2$  for a residence time of 2 h. The analytical data are listed in the Table.

Comparative Example C1 (non-inventive; aim:  
same carbon content as Example 1 but different silica)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 100 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK<sup>®</sup> N10 from Wacker-Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 2.56 g of a mixture of 0.56 g of H<sub>2</sub>O and 2.0 g of MeOH and 4.29 g of dimethyldichlorosilane (2.56 g of the mixture contains 1.60g of DMDCS). The silica thus loaded is reacted at 250°C in a 100 L drying cabinet under N<sub>2</sub> for a residence time of 2 h. The analytical data are listed in the Table.

Example 3 (non-inventive; aim:  
same carbon content as Example 1 but different organosilicon compound)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 200 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK<sup>®</sup> N20 from Wacker-Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 8.21 g of a mixture of 1.79 g of H<sub>2</sub>O and 6.42 g of MeOH and 9.90 g of methyltrichlorosilane (8.21 g of the mixture contains 4.49g MTCS). The silica thus loaded is reacted at 250°C in a 100 L drying cabinet. The analytical data are listed in the Table.

Example 7 (2.1 parts of silylating agent)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 200 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and

66132) available under the name HDK<sup>®</sup> N20 from Wacker Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 0.35 g of H<sub>2</sub>O and 2.10 g (*i.e.* 2.1 parts with respect to silica; 0.09 mmol/g per 100 m<sup>2</sup>/g silica of trimethylsiloxy groups) of trimethylethoxysilane. The silica thus loaded is reacted at 200°C in a 100 l drying cabinet under N<sub>2</sub> for a residence time of 2 h. The analytical data are listed in Table 1.

Comparative Example C3 (2.1 parts of silylating agent)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 100 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK<sup>®</sup> N20 from Wacker Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 0.47 g of H<sub>2</sub>O and 2.10 g (*i.e.*, 2.1 parts with respect to silica; 0.18 mmol/g per 100 m<sup>2</sup>/g silica of trimethylsiloxy groups) of hexamethyldisilazane. The silica thus loaded is reacted at 80°C in a 100 l drying cabinet under N<sub>2</sub> for a residence time of 2 h and then cleaned from by-products at 150°C for 1 h. The analytical data are listed in the Table.

Comparative Example C4 (2.1 parts of silylating agent and lower BET surface area)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 100 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK<sup>®</sup> C10 from Wacker Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 0.35 g of H<sub>2</sub>O and 2.10 g (*i.e.*, 2 parts with respect to silica; 0.09 mmol/g per 100 m<sup>2</sup>/g silica of trimethylsiloxy groups) of trimethylethoxysilane. The silica thus loaded is reacted at 200°C in a 100 l drying cabinet under N<sub>2</sub> for a resistance time of 2 h. The analytical data are listed in Table 1.



Table 1

Example	Silica Surface Area (m <sup>2</sup> /g)	Silylating Agent, wt. %	Carbon Content wt. %	% SiOH	Water Wettable?	Methanol Number
1	200	1.07 DMDCS	0.56	80	yes	0
2	300	2.67 HMDS	0.95	82	yes	5
3	150	1.33 HMDS	0.41	74	yes	15
4	200	1.00 OH-PDMS	0.35	94	yes	0
5	200	2.00 OH-PDMS	0.61	84	yes	0
6	200	1.60 DMDCS	0.82	71	yes	0
C1	100	2.56 DMDCS	0.85	43	no	45
C2	200	4.49 MTCS	0.81	48	no	40
7	200	2.10 TMES	0.54	72	yes	0
C3	100	2.10 HMDS	1.13	55	no	43
C4	100	2.10 TMES	0.58	44	no	52
Barthel 1	200	32 DMDCS	3.0	Not Detectable	no	55
Barthel 2 (Comparative)	200	32 DMDCS	1.5	Detectable	no	40
Subj. Inv.	25 - 500	0.015 - 0.15 mmol/g	> 0 to 2.0	Surface Silanol 0.9 - 1.7 SiOH/nm <sup>2</sup>	yes	< 30
Barthel	25 - 400+	2 - 100 wt. %	> 1 to 2+	0 (col. 1, ll. 44-49)	no	> 50

The conclusions which can be drawn from the table are evident. For example, it is clear that there is no relationship between carbon content and methanol number. Looking at Examples 2 and 3, the same silylating agent was used. Since the silica of Example 3 had only half the specific surface area of the silica of Example 2, half the amount of silylating agent was



used. However, neither the surface silanol content nor the methanol numbers are similar. Example 2 contained 0.95% carbon and had a methanol number of 5, while Example 3 had a carbon content of 0.41% and a higher methanol number (more hydrophobic), but still well within the scope of the claims (methanol number of 15).

Example 7 and Comparative Example C4 employed the same silylating agent, in the same amounts. Only the silica particle size is different. Comparative Example C4 meets *Barthel's* requirement of a methanol number  $\geq 50$ , but Example 7 does not. Rather, it has a methanol number of zero, meeting Appellants' claim limitation of a methanol number  $< 30$ . Note that the carbon content of both silicas is similar.

All the subject invention examples employ relatively low amounts of silylating agent, between 0.015 and 0.15 mmol/g per 100 m<sup>2</sup>/g of silica surface area, which is an important claim limitation. Each example had a low methanol number, most of them zero, while the carbon content fluctuated between 0.35 weight percent and 0.95 weight percent. Contrast these with the silicas of *Barthel*. The Barthel 1 silica (Example 1 of *Barthel*) and the comparative example (Comparative Example 2 of *Barthel*) both employed the same silica, with identical surface area (200 m<sup>2</sup>/g), the same silylating agent (dimethyldichlorosilane), and the same amount of silylating agent (32 weight percent). Yet the silicas had quite different properties. The Barthel 1 silica (his inventive silica) had no detectable surface silanol groups (IR band, DRIFT), while the comparative example did. Also, despite the same amount of silylating agent having been added, the comparative silica had half the carbon content (1.5 weight %) than the inventive silica (3.0 weight %). Both silicas are well outside Appellants' claims, with methanol numbers of 55 and 40, respectively. These experiments from the prior art make clear what Appellants have stated earlier. Merely because the same amount of silylating agent is used, with the same silica, there is still no relationship between these facts and the silanol content or methanol number, or even the carbon content. In this case, one silylation was performed initially at a low temperature using

a mist of silylating agent, while the other employed a higher temperature with the silylating agent in gaseous form.

Thus, the Office's conclusions that:

Clearly, the degree of hydrophobicity of silylated silica would depend upon the amount of silylating agent . . . .

is incorrect. *Barthel*'s own examples bear this out. But more importantly, *Barthel* does not teach or suggest using a low amount of silylating agent to obtain a silica having a methanol number  $< 30$ . He does teach using an amount of silylating agent (a very large amount, generally) to obtain a silica having a methanol number  $\geq 50$ . It would not be obvious to prepare a partly hydrophobic silica with a methanol number of less than 30. That is Appellants' invention, not that of *Barthel*. *Barthel* teaches not to do this.

The Declaration of Dr. Gottschalk-Gaudig also attests to the fact that it is well known to the skilled artisan that merely because silylating/silica or carbon content/silica ratios are the same, this is no indication that the silica will have the same properties. See, for example, paragraph 7 - 9 of the Declaration. In the Advisory Action, the Examiner states: "Appellants did not show why Barthel's pyrogenic silica of 200m<sup>2</sup>/g treated with less than 2.86 wt.% of DMDCS should have a methanol number of less than 30." (Advisory Action, page 3). This is incorrect. Appellants have shown this by actual example. In Example 1, 2.86g of a mixture of DMDCS was used to prepare a partly hydrophobic silica. The mixture contained 1.07 g DMDCS/100 g silica (1.07 g of the 2.86g mixture). The silica had a methanol number of 0. In Example 6, a higher amount, 1.6 g DMDCS/100 g of 200 m<sup>2</sup>/g silica was used. This silica also had a methanol number of 0. The reason why these silicas have such a low methanol number is that they meet the claim limitation of using 0.05 to 0.15 mmol (millimol) of silylating agent per gram of silica per 100 m<sup>2</sup>/g surface area. *Barthel* uses very high amounts. From the actual examples, the use of small amounts of silylating agent (0.015 mmol/g to 0.15 mmol/g) per 100 m<sup>2</sup>/g surface area)

factually does not create a *Barthel* silica. These are actual examples; evidentiary facts which cannot be disputed.

*Barthel* discloses a wide range of silylating agent amount because silica has both a varying silanol surface density ( $\text{SiOH}/\text{nm}^2$  of surface area) as well as a varying surface area (e.g.  $25\text{m}^2/\text{g}$  to  $400^+\text{m}^2/\text{g}$ ). *Barthel* discloses a wide range to ensure that silica meeting his requirements can always be produced: methanol number  $>50$ , no detectable silanol groups, highly or totally apolar.

If indeed one could pick and choose from among the many independent variables disclosed by *Barthel* and thereby produce a subject invention silica having a methanol number  $< 30$ , such picking and choosing is irrelevant to patentability. *Barthel* teaches against doing so. He proposes wide ranges of variables to take into account the differences between, *inter alia*, silica specific surface area; number of surface silanol groups (in  $\text{SiOH}/\text{nm}^2$ ) of a silica with a defined surface area; type and reactivity of silylating agent; molecular weight of silylating agent; loading temperature of silylating agent; loading method for silylating agent; reaction temperature and duration of reaction for silylation; continuous or stepped reaction temperature; post-treatment of silylated silica; addition or non-addition of co-reactants (e.g., water, methanol); amount of co-reactants, etc. Of all these variables, there is absolutely no direction provided by *Barthel* to choose parameters which would not work to make his silica: completely hydrophobicized silica with no detectable surface silanol groups, having a methanol number  $\geq 50$ . *Barthel* teaches away from the claimed invention. Reversal of the rejection over *Barthel* is respectfully solicited.

**C. The Claims Are Patentable Over Tojo**

*Tojo* is not directed to the problem solved by Appellants' i.e. providing partly hydrophobic silica particles which have the ability to act as dispersants and emulsifiers. Rather *Tojo* is directed to a field somewhat similar to that of *Barthel*: providing highly hydrophobic

silica particles which can be used in ethylene/ $\alpha$ -olefin rubber, which, as can be seen is a highly hydrophobic matrix, the rubber displaying enhanced aging resistance (*e.g.* freedom from crepe hardening). The difference between *Barthel* and *Tojo* is that *Tojo* blocks the surface silanol groups with silanes which contain alkenyl, chloroalkenyl, or chloroalkyl groups, because these specific functional groups can react with the unsaturated groups remaining in the rubber during vulcanization, thus bonding the silica particles to the rubber matrix. Indeed, the silanes are termed by *Tojo* as "coupling agents." *Tojo* does not teach or suggest the claimed invention, which requires 0.9 to 1.7 SiOH groups/nm<sup>2</sup> of surface. As can be clearly seen, *Tojo's* desire is not only to eliminate all surface silanol groups (by selecting a silica which already has a low silanol content), but to eliminate these groups by derivatizing with specific hydrophobic groups which are reactive with the rubber, i.e. can serve as "coupling agents."

As indicated previously during prosecution of this application, *Tojo* does not disclose, teach, or suggest the claimed partly hydrophobic silicas. In assessing the issue of obviousness over the prior art, it is well-established that the claim must be viewed as a whole. Claim 15 contains numerous claim limitations, of which the most important ones, for the purposes of this discussion, are as follows:

- (1) contact angle  $\theta < 180^\circ$ ;
- (2) degree of coverage  $1\% < \tau < 50\%$ ;
- (3) density of surface silanol groups  $\geq 0.9$  and  $\leq 1.7$  SiOH/nm<sup>2</sup>;
- (4) carbon content  $> 0$  and less than 2 wt. %;
- (5) methanol number  $< 30$ ;
- (6) amount of silylating agent 0.015 to 0.15 mmol/g per 100 m<sup>2</sup>/g silica surface area.

All these requirements must be simultaneously met. *Tojo* discloses only one of these six limitations in some manner or other:

(4) carbon content,

and vaguely mentions only one further silica characteristic:

(3) existence of surface silanol groups, prior to silylation.

With respect to limitation (3), the only mention of silanol content in the entire specification of *Tojo* reads as follows:

Among various silica type fillers, dry method silica has a relatively low silanol group content, and if this silica is treated with the above-mentioned silane, the silanol group is blocked and it is considered that the silica is effectively bonded to the rubber by the functional group of the silane.

*Tojo*, column 5, lines 10-15 (emphasis added). There is no other reference to silanol groups in the entire *Tojo* specification, and this sole passage indicates blockage of the silanol groups, *i.e.*, a surface silanol group content of 0 SiOH/nm<sup>2</sup>. Appellants' claims require 0.9 to 1.7 SiOH/nm<sup>2</sup>, a still very appreciable number of silanol groups. Thus, this limitation is not disclosed by *Tojo*.

With regard to limitation (4), *Tojo* discloses carbon contents of 0.1 to 5% by weight, preferably 0.5 to 4%, and especially preferably 1 to 3% by weight (col. 5, lines 16-20). Thus, the range disclosed by *Tojo* encompasses Appellants' claimed range of > 0 and less than 2 weight %. This is the only one of the six limitations listed above which is disclosed by *Tojo*. However, as indicated previously, there is no direct relationship between this variable and methanol number, silanol content, etc. This is borne out by the Declaration of Dr. Gottschalk-Gaudig.

When a reference does not disclose or suggest one or more claim limitations, the claimed invention cannot be rejected over the reference unless the remaining claim limitations

are inherent. This has been the law for many years. However, for inherency to apply, the rejection must be for anticipation under 35 U.S.C. § 102, and the inherent feature relied upon must be a certain and necessary result, *i.e.*, one which occurs of necessity, 100% of the time, and not just a possibility or even a probability. *See, e.g., Ex parte McQueen*, 123 USPQ 37 (POBA 1958); *Ex parte Cyba*, 155 USPQ 756 (POBA 1966); *Ex parte Keith*, 154 USPQ 320 (POBA 1966); and especially *In re Robertson*, 49 USPQ2d 1949 (Fed. Cir. 1999).

Inherency is immaterial to a rejection for obviousness under 35 U.S.C. § 103. If the reference does not disclose, teach, or suggest even a single claim limitation, this limitation cannot be supplied based on surmise, *i.e.*, that it may occur or even probably will occur. These are arguments based on inherency, and as stated, inherency is immaterial to obviousness. *See, e.g., In re Shetty*, 195 USPQ 753 (CCPA 1977); *In re Naylor*, 152 USPQ 106 (CCPA 1966); *In re Spormann*, 150 USPQ 449 (CCPA 1966); *Jones v. Hardy*, 230 USPQ 1021, 1025 (Fed. Cir. 1984).

Here, this is just the argument made by the Office. The rejection is for obviousness under 35 U.S.C. § 103(a). The Office first postulates the following statement:

In other words, some silica treated by the method of Tojo would be substantially identical to that of the claimed invention and some of the treated silica would not be substantially identical to that of the claimed invention.

This statement alone is clear evidence that the silica of *Tojo* does not inherently possess Appellants' claim limitations.

In an attempt to escape the rigors of the doctrine of inherency, the Office states, without legal support, that "the 102 principles of inherency was not applied." However, inherency was applied. The only way a rejection can be made over a prior art reference which



does not disclose a claim limitation is under principles of inherency, and as stated in *In re Evanega*, 4 USPQ2d 1249 (Fed. Cir. 1987), when evaluating obviousness, all claim limitations must be evaluated, and must be disclosed, taught, or suggested by the reference:

In this respect, the mere absence from the reference of an explicit requirement of the claim cannot reasonably be construed as an affirmative statement that the requirement is in the reference.

*Evanega* at 1251. In other words, since *Tojo* does not disclose five of the six limitations discussed, it cannot be assumed that these limitations are met. *Evanega* is controlling law.

The Office cites *In re Malagari*, 182 USPQ 549 (CCPA 1974), as standing for the proposition that "it is well settled that overlapping ranges are *prima facie* evidence of obviousness." As a broad statement, this is incorrect. Moreover, *Malagari* does not apply to the present case<sup>2</sup>.

In *Malagari*, the invention was directed to a ten step process for preparing grain-oriented silicon steel for use in transformer cores and motor cores, the steels produced by the claimed process, which produced silicon steel characterized in lower hysteresis loss and higher magnetic permeability. The claims were rejected under 35 U.S.C. § 103 over the *Goss* reference. *Goss* unambiguously disclosed nine of the ten claim limitations exactly, in other words, every claim limitation except one. In that single different limitation, the first step of the claimed process, steel which contained from 0.03 to 0.07 weight % carbon is heated. *Goss* disclosed 0.02 to 0.03% carbon in an otherwise identical step.<sup>3</sup>

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<sup>2</sup>It is believed that the Office intends *Malagari* to apply to the rejection over *Barthel* as well, but it does not, for the same reasons given with respect to *Tojo*.

<sup>3</sup>Under present law, the claim would have been anticipated since the endpoint of the *Goss* range and the claimed range are the same, i.e. the ranges touch.



Thus, unlike the present case, where there are many limitations, including the six discussed here, five of which are not disclosed by the reference. In *Malagari*, there was only a single limitation not explicitly disclosed by the prior art, a range of 0.03 to 0.07%, but the lower end of that range touched the high end of the reference's range. When there are multiple limitations claimed, meeting only one such limitation by means of an overlap of ranges is not sufficient, and does not create a case of *prima facie* obviousness. All limitations must be met. This case is completely different from that in *Malagari*, and *Malagari* does not apply.

Moreover, as the examples and comparative examples show, with respect to the carbon content, merely because some of the prior art ranges are within the claimed range does not imply that the remaining claim limitations are met. For example, the table on page 16 clearly indicates that there is no direct relationship between carbon content and any of the remaining properties.

Finally, it must be noted that even if the broad ranges of *Tojo*'s silica specific surface area, carbon content, etc. would allow the preparation of a silica meeting all of Appellants' claim limitations, *Tojo* provides no teaching or suggestion, no direction, no motivation to produce a silica which is only partly hydrophobicized and still contains large amounts of silanol groups. It is Appellants who teach doing so, not *Tojo*. Appellants did so to provide silica particles with surfactant-like behavior, a problem not discussed by *Tojo* and not remotely relevant to any of *Tojo*'s rubber compositions. There must be some teaching or suggestion in the reference to do as Appellants have done. *Tojo* has none, and the Office has not pointed to any such teaching or suggestion. *See, e.g., Ex parte Kuhn*, 132 USPQ 359 (POBA 1961), where the Board stated that although the inventor (Kuhn) was working within the broad range of the prior art, it was improper to reject the claims over the art when to arrive at the claimed invention would require selecting specific items and conditions from the prior art, when the reference failed to give some directions or reasons for making the selection.

Finally Appellants note that the silylating agents of *Tojo* are very specific, in order that these might adhere to or bond with the rubber matrix. In order to do so, the silylating agents must have alkenyl, chloroalkenyl, or chloroalkyl functional groups to react with the diene rubber.

Claim 16 requires the silylation to be performed with an organopolysiloxane. This is not optional in claim 16; it is required. *Tojo* employs only silanes, not organosiloxanes, and does not teach or suggest using these silylating agents. Claim 16 is separately patentable over *Tojo*.

Claim 18 requires hydrosilylation with both a silane and an organosiloxane. *Tojo* does not teach or suggest this. Claim 18 is separately patentable over *Tojo*.

Claim 19 requires that the silane of claim 17 have R<sup>1</sup> groups selected from the group consisting of the enumerated alkyl, aryl, and alkylaryl radicals. *Tojo* requires an alkenyl radical, a chloroalkenyl radical, or a chloroalkyl radical. In column 1, *Tojo* cites prior art silicas which have been silylated with trimethylchlorosilane, and indicates that these silicas are not acceptable in diene rubber. *Tojo* does not teach or suggest the subject matter of claim 19, which is separately patentable, but rather teaches away. Claim 19 is separately patentable over *Tojo*.

Claim 33 requires the silylation to be performed with one or more silanes selected from the group consisting of methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, or hexamethyldisilazane. None of these bear *Tojo*'s required functional groups, and none are taught or suggested by *Tojo*. Claim 33 is separately patentable over *Tojo*. Appellants do not understand the comment of the Office relative to this claim as set forth at the bottom of page 5 of the Office Action of December 10, 2008. All of the compounds of claim 33 are silanes, as are also the compounds of claim 17, which are required ("silylating is performed"), not optional.


Reversal of the rejections of all the claims over *Tojo* is respectfully solicited.

In summary, both of the prior art references teach the use of highly hydrophobic silicas where all surface silanol groups are blocked. Such silicas, with high methanol numbers, do not fall within the scope of the claims, which require a methanol number less than 30. *Barthel* teaches against using a silica with a methanol number less than 50. Teaching away is strong evidence of non-obviousness. All the claims are patentable.

The fee of \$540.00 as applicable under the provisions of 37 C.F.R. § 41.20(b)(2) is being charged to Deposit Account No. 02-3978 via electronic authorization submitted concurrently herewith. Please charge any additional fee or credit any overpayment in connection with this filing to our Deposit Account No. 02-3978.

Respectfully submitted,

**Torsten Gottschalk-Gaudig et al.**

By:   
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Registration No. 31,209  
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Date: May 11, 2009

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Enclosure - Appendices

### VIII. CLAIMS APPENDIX

Claims 1 - 14. (Cancelled).

15. Partly hydrophobic silica particles, said partly hydrophobic silica particles having a contact angle  $\theta$  in air for water of less than  $180^\circ$ , a degree of coverage  $\tau$  of the surface of the silica with silylating agent residues, based on the total silica particle surface area, of  $1\% < \tau < 50\%$ , a density of surface silanol groups SiOH ranging between a minimum of 0.9 and a maximum of 1.7 SiOH/nm<sup>2</sup> particle surface area, and having a carbon content of more than 0% and up to 2.0% by weight, and a methanol number of less than 30, said partly hydrophobic silica prepared by a process comprising silylating silica particles prepared under anhydrous conditions, with

I) an organosilane of the formula



where n is 1, 2 or 3

or mixtures of these organosilanes,

$R^1$  being a monovalent, optionally halogenated hydrocarbon radical having 1 to 24 carbon atoms, being identical or different at each occurrence, and being saturated, aromatic, monounsaturated, or polyunsaturated,

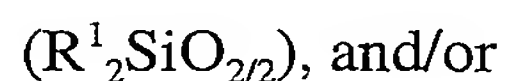
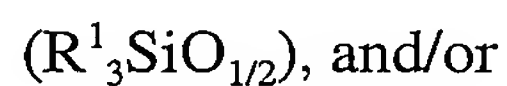
X each independently being halogen, a nitrogen radical,  $\text{OR}^2$ ,  $\text{OCOR}^2$ , or  $\text{O}(\text{CH}_2)_x\text{OR}^2$ ,

$\text{R}^2$  being hydrogen or a monovalent hydrocarbon radical having 1 to 12 carbon atoms, and

x being 1, 2 or 3;

or

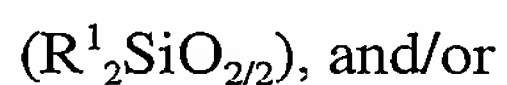
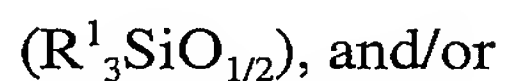
II) an organosiloxane composed of units of the formula



where  $\text{R}^1$  is as defined above, or mixtures thereof,

the number of these units in one organosiloxane being at least 2; and I and II being used alone or in any desired mixtures in a total amount of from 0.015 mmol/g to 0.15 mmol/g per 100 m<sup>2</sup>/g of silica BET surface area measured by the BET method in accordance with DIN 66131 and 66132.

16. The particles of claim 15, wherein said silylating is performed with an organosiloxane composed of units of the formula (II)





where  $R^1$  is as defined above, or mixtures thereof,

the number of these units in one organosiloxane being at least 2;  $\Pi$  being used in a total amount of from 0.015 mmol/g to 0.15 mmol/g per 100 m<sup>2</sup>/g of silica BET surface area measured by the BET method in accordance with DIN 66131 and 66132.

17. The particles of claim 15, wherein said silylating is performed with an organosilane of the formula



where n is 1, 2, or 3, or a mixture of these organosilanes, where  $R^1$  is a C<sub>1-24</sub> hydrocarbon radical selected from the group consisting of alkyl radicals, alkenyl radicals, aryl radicals, and alkylaryl radicals, each  $R^1$  being the same or different,

X each independently being halogen, a nitrogen radical, OR<sup>2</sup>, OCOR<sup>2</sup>, or

O(CH<sub>2</sub>)<sub>x</sub>OR<sup>2</sup>,

R<sup>2</sup> being hydrogen or a monovalent hydrocarbon radical having 1 to 12 carbon atoms, and

x being 1, 2 or 3.

18. The particles of claim 17, wherein said step of silylating is performed with a mixture of at least one organosilane of the formula  $R^3_nSiX_{4-n}$  with an organosiloxane of the formula (II).

19. The particles of claim 17, wherein each  $[R^3]$   $R^1$  individually is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, decyl, dodecyl, hexadecyl, octadecyl, phenyl, biphenyl, naphthyl, benzyl, ethylphenyl, tolyl, and xylyl radicals.

20. - 29. (Cancelled).

30. The particles of claim 15, wherein said partly hydrophobic silica has a methanol number less than 20.

31. The particles of claim 15, wherein said partly hydrophobic silica has a carbon content of 0.1 to 0.5 weight percent per each 100 m<sup>2</sup>/g of surface area.

32. The composition of claim 17, wherein  $R^1$  is independently selected from the group consisting of methyl, octyl, and vinyl.



33. The partly hydrophobic silica particles of claim 17, wherein at least one organosilane is selected from the group consisting of methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, and hexamethyldisilazane.

34. The partly hydrophobic silica particles of claim 15, wherein the contact angle  $\theta$  is between  $100^\circ$  and  $0^\circ$ .

35. The partly hydrophobic silica particles of claim 15, wherein the contact angle  $\theta$  is between  $90^\circ$  and  $0^\circ$ .

36. The partly hydrophobic silica particles of claim 15, wherein the density of surface silanol groups is between 1.2 and 1.7 SiOH per  $\text{nm}^2$  of particle surface.

## **IX. EVIDENCE APPENDIX**

### **1. Gottschalk Gaudig Declaration**

**X. RELATED PROCEEDINGS APPENDIX**

**None.**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

Torsten Gottschalk-Gaudig et al.

Serial No.: 10/738,543

Filed: December 17, 2003

For: WATER-WETTABLE SILYLATED METALOXIDES

Attorney Docket No.: WAS 0611 PUS

Group Art Unit: 1792

Examiner: Elena Tsoy Lightfoot

DECLARATION OF DR. TORSTEN GOTTSCHALK-GAUDIG

Mail Stop Amendment  
Commissioner for Patents  
U.S. Patent & Trademark Office  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Dr. Torsten Gottschalk-Gaudig, do hereby declare and state as follows:

1. I studied organic chemistry and coordination chemistry from 1987 to 1994 at the Universität Erlangen-Nürnberg, and from 1994 to 1997 pursued my doctoral studies, under the supervision of Prof. D. Sellmann, Institut für Anorganische Chemie II, at the same university. I achieved my Ph.D *summa cum laude*, my thesis titled "Activation and Stabilization of Small Molecules by Ruthenium Complexes Bearing Tetradentate Thioether-Thiolate Ligands. I pursued post doctoral studies under Prof. K.G. Caulton at Indiana University during 1998 to 1999, and then under Prof. Sellmann at the Universität Erlangen-Nürnberg during 1999-2000. In November of 2000 I accepted the position of Research and Development Manager, SILICA, at Wacker Chemie AG, and since June of 2003 I have been Platform Manager, SILICA, for that company. I am the author or co-author of some 26 scientific publications, and am a named inventor for numerous patent families filed worldwide. A list of publications and patent families is attached.

2. I am a coinventor of the subject matter disclosed and claimed in U.S. Patent Application Serial No. 10/738,543, and am familiar with the subject matter of the

application, the Office Actions received from the United States Patent and Trademark Office, and the references cited by the Patent Examiner.

3. The *Barthel* reference, U.S. 5,686,054 discloses a method of producing silica with exceptionally high hydrophobicity and zero detectable surface silanol content. *Barthel* requires the silica to have a methanol number  $\geq 50$ .

4. Very hydrophobic silicas are important in the processing of silica-filled hydrophobic polymers, as they are easily incorporated into the polymer, for example in a single or twin screw mixer, Banbury mixer, kneading cascade, or the like. In contrast, hydrophilic silicas are difficult to incorporate, and at high filler levels can produce dry-appearing crumb which is difficult or impossible to further process. Therefore, the aim of Dr. Barthel was to increase the hydrophobicity to as high a level as possible. This was accomplished by a specific process where the silica is loaded with silylating agent in the form of a mist at relatively low temperature, followed by reaction at a much higher temperature.

5. Dr. Barthel recognized that the amounts of silylating agent could vary over a relatively wide range, a range which is dependent upon such factors as type of silylating agent, type of silica, surface area of silica, and specific processing method. Some silylating agents can also react with previously bonded silyl groups rather than silanol groups. However, while the ranges are necessarily broad, they are only broad so as to enable one skilled in the art to produce a "*Barthel*" silica, i.e. one with a very high methanol number, one which is highly hydrophobic and has no detectable silanol groups. *Barthel* would not motivate one skilled in the art to produce only a partly hydrophobicized silica. *Barthel* teaches only fully hydrophobicized silica.

6. *Tojo* has also been cited by the Examiner. One skilled in the art, reading *Tojo*, understands that *Tojo* wishes all the silanol groups of untreated silica to be "blocked" by silyl groups bearing functional groups which can bond to the diene rubber of *Tojo*. *Tojo* does not disclose any silica having a low methanol number or low surface silanol content. *Tojo* contrasts his specific silyl functional groups with other silyl groups such as trimethylsilyl groups, because the latter do not provide sufficient aging resistance. Thus, *Tojo* requires the silyl "functional" groups to be alkenyl, chloroalkenyl, or chloroalkyl groups.

7. The Examiner appears to believe that if the carbon content of the claimed silica is within the carbon content range of *Barthel* or *Tojo*, that the remaining claimed properties, e.g. surface coverage, wetting angle, surface silanol group content, and methanol content will also be met. This is incorrect, as is well known to the skilled artisan, and is borne out even by the Examples of *Barthel*. *Barthel's* Example 1 and Example 2 (comparative) silicas were both prepared from the same type of silica, with the same specific surface area, the same silylating agent, and the same amount of silylating agent. Yet, the Comparative Example had half the carbon content of the *Barthel*-processed silica, and a lower methanol number, although still very high.

8. To further illustrate that there is no direct relationship between carbon content, silanol content, and methanol number, a series of Examples and Comparative Examples were prepared under my direction, in the laboratories of Wacker Chemie A.G. in Burghausen, Germany. These examples are set forth in the Table on the next page, and employ various silylating agents, in various amounts, with silicas of different surface areas. In the Table, the silylating agents used are identified as follows:

DMDCS	dimethyldichlorosilane
HMDS	hexamethyldisilazane
OH-PDMS	hydroxyl-terminated-polydimethylsiloxane
MTCS	methyltrichlorosilane
TMES	trimethylethoxysilane.

Both HMDS and TMES result in formation of  $(\text{CH}_3)_3\text{Si-O}$  groups on the silica surface, and in this respect these silylating agents are similar.

The details of the additional examples/comparative examples are as follows. The details for Examples 1-5 may be found in the specification.

Example 6 (according to the invention)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 200 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK® N20 from Wacker-Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 2.56 g of a mixture of 0.56 g of H<sub>2</sub>O and 2.0 g of MeOH and 4.29 g of dimethyldichlorosilane. The silica thus loaded is reacted at 250°C in a 100 L drying cabinet under N<sub>2</sub> for a residence time of 2 h. The analytical data are listed in the Table.

Comparative Example C1 (non-inventive; aim:  
same carbon content as Example 1 but different silica)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 100 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK® N10 from Wacker-Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 2.56 g of a mixture of 0.56 g of H<sub>2</sub>O and 2.0 g of MeOH and 4.29 g of dimethyldichlorosilane. The silica thus loaded is reacted at 250°C in a 100 L drying cabinet under N<sub>2</sub> for a residence time of 2 h. The analytical data are listed in the Table.

Example 3 (non-inventive; aim:  
same carbon content as Example 1 but different organosilicon compound)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 200 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK® N20 from Wacker-Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 8.21 g of a mixture of 1.79 g of H<sub>2</sub>O and 6.42 g of MeOH and 9.90 g of methyltrichlorosilane. The silica thus loaded is reacted at 250°C in a 100 L drying cabinet. The analytical data are listed in the Table.



Example 7 (2.1 parts of silylating agent)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 200 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK<sup>®</sup> N20 from Wacker Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 0.35 g of H<sub>2</sub>O and 2.10 g (*i.e.* 2.1 parts with respect to silica; 0.09 mmol/g per 100 m<sup>2</sup>/g silica of trimethylsiloxy groups) of trimethylethoxysilane. The silica thus loaded is reacted at 200°C in a 100 l drying cabinet under N<sub>2</sub> for a residence time of 2 h. The analytical data are listed in Table 1.

Comparative Example C3 (2.1 parts of silylating agent)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 100 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK<sup>®</sup> N20 from Wacker Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 0.47 g of H<sub>2</sub>O and 2.10 g (*i.e.*, 2.1 parts with respect to silica; 0.18 mmol/g per 100 m<sup>2</sup>/g silica of trimethylsiloxy groups) of hexamethyldisilazane. The silica thus loaded is reacted at 80°C in a 100 l drying cabinet under N<sub>2</sub> for a residence time of 2 h and then cleaned from by-products at 150°C for 1 h. The analytical data are listed in the Table.

Comparative Example C4 (2.1 parts of silylating agent and lower BET surface area)

At a temperature of 25°C and under N<sub>2</sub> inert gas, 100 g of hydrophilic silica with a moisture content of less than 1%, an HCl content of less than 100 ppm, and with a specific surface area of 100 m<sup>2</sup>/g (measured by the BET method in accordance with DIN 66131 and 66132) available under the name HDK<sup>®</sup> C10 from Wacker Chemie AG, Munich, Germany, are mixed by atomization through a one-fluid nozzle (pressure: 5 bar) with 0.35 g of H<sub>2</sub>O and 2.10 g (*i.e.*, 2 parts with respect to silica; 0.09 mmol/g per 100 m<sup>2</sup>/g silica of trimethylsiloxy groups) of

trimethylethoxysilane. The silica thus loaded is reacted at 200°C in a 100 l drying cabinet under N<sub>2</sub> for a residence time of 2 h. The analytical data are listed in Table 1.

Table 1

Example	Silica Surface Area (m <sup>2</sup> /g)	Silylating Agent, wt. %	Carbon Content wt. %	% SiOH	Water Wettable ?	Methanol Number
1	200	2.86 DMDCS	0.56	80	yes	0
2	300	2.67 HMDS	0.95	82	yes	5
3	150	1.33 HMDS	0.41	74	yes	15
4	200	1.00 OH-PDMS	0.35	94	yes	0
5	200	2.00 OH-PDMS	0.61	84	yes	0
6	200	2.56 DMDCS	0.82	71	yes	0
C1	100	2.56 DMDCS	0.85	43	no	45
C2	200	9.90 MTCS	0.81	48	no	40
7	200	2.10 TMES	0.54	72	yes	0
C3	100	2.10 HMDS	1.13	55	no	43
C4	100	2.10 TMES	0.58	44	no	52
Barthel 1	200	32 DMDCS	3.0	Not Detectable	no	55
Barthel 2 (Comparative)	200	32 DMDCS	1.5	Detectable	no	40
Subj. Inv.	25 - 500	0.015 - 0.15 mmol/g	> 0 to 2.0	Surface Silanol 0.9 - 1.7 SiOH/nm <sup>2</sup>	yes	≥ 30
Barthel	25 - 400+	2 - 100 wt. %	> 1 to 2+	0 (col. I, II. 44-49)	no	> 50

9. One can see from these results that there is no relationship between carbon content, and for example, methanol number. The values of many parameters are specified in the claim. Six of these, for example, are

- (1) contact angle  $\theta < 180^\circ$ ;
- (2) degree of coverage  $1\% < \tau < 50\%$ ;
- (3) density of surface silanol groups  $\geq 0.9$  and  $\leq 1.7$  SiOH/nm<sup>2</sup>;
- (4) carbon content  $> 0$  and less than 2 wt. %;
- (5) methanol number  $< 30$ ;
- (6) amount of silylating agent 0.015 to 0.15 mmol/g per 100 m<sup>2</sup>/g silica surface area.

Each of these must be simultaneously met; not just one, and meeting only one limitation does not infer that any or all of the others are necessarily met. For example, Comparative Examples C1, C2, C3, and C4 all meet the carbon content limitation, with carbon contents ranging from 0.58 to 1.13 weight percent, yet none of these silicas meet Applicants' claim requirement of a methanol number  $< 30$ . Asserting that if one limitation is met, all others are met, is somewhat like stating that someone has won the lottery when only one of his six numbers matched the drawn numbers.

10. Not only do neither *Barthel* or *Tojo* disclose any silica falling within Applicants' claims, most importantly, both direct the skilled artisan away from the claimed silica. One skilled in the art, reading *Tojo* and *Barthel*, would be motivated to select the silylating conditions so as to produce only silicas with a very high methanol number. Both these references direct the skilled artisan in a direction opposed to what Applicants have done.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

  
Dr. Torsten Gottschalk-Gaudig et al.

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## List of publications:

### Scientific Publications:

1. Ridaoui, H.; Donnet, J.-B.; Balard, H.; Kellou, H.; Hamdi, B.; Barthel, H.; Gottschalk-Gaudig, T.; Legrand, A.-P. Colloids and Surfaces, A: Physicochemical and Engineering Aspects (2008), 330(1), 80-85
2. Donnet, J.-B.; Balard, H.; Nedjari, N.; Hamdi, B.; Barthel, H.; Gottschalk-Gaudig, T. Journal of Colloid and Interface Science (2008), 328(1), 15-19
3. Kaetzel, U.; Gottschalk-Gaudig, T.; Stintz, M.; Barthel, H. Chemie Ingenieur Technik (2008), 80(9), 1408
4. Kellou, H.; Hamdi, B.; Brendle, E.; Gottschalk-Gaudig, T.; Barthel, H.; Ridaoui, H.; Balard, H.; Donnet, J.-B. Colloids and Surfaces, A: Physicochemical and Engineering Aspects(2008), 327(1-3), 90-94
5. Donnet, J.-B.; Ridaoui, H.; Balard, H.; Barthel, H.; Gottschalk-Gaudig, T. Journal of Colloid and Interface Science (2008), 325(1), 101-106
6. Kaetzel, U.; Vorbau, M.; Stints, M.; Gottschalk-Gaudig, T.; Barthel, H. Particle & Particle Systems Characterization (2008), 25(1), 19-30
7. Kaetzel, U.; Bedrich, R.; Stintz, M.; Ketzmerick, R.; Gottschalk-Gaudig, T.; Barthel, H. Particle & Particle Systems Characterization (2008), 25(1), 9-18
8. Gottschalk-Gaudig, T.; Barthel, H. Organosilicon Chemistry VI: From Molecules to Materials (2005), Volume 2, 902-909.
9. Zhuang, Y.; Sampurno, Y. A.; Sudargho, F.; Steward, G.; Barthel, H.; Mayer, E.-P.; Gottschalk-Gaudig, T.; Stintz, M.; Kaetzel, U.; Nogowski, A.; Goldstein, M.; Philipossian, A. Materials Research Society Symposium Proceedings (2007), 991(Advances Challenges in Chemical Mechanical Planarization), 233-238
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12. Dreyer, M.; Gottschalk-Gaudig, T.; Barthel, H. European Coatings Journal (2007), (7-8), 39-44
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14. Dreyer, M.; Gottschalk-Gaudig, T.; Barthel, H. Farbe + Lack (2007), 113(4), 28-129
15. Kaetzel, U.; Stintz, M.; Babick, F.; Barthel, H.; Gottschalk-Gaudig, T. AIChE Spring National Meeting, Conference Proceedings, Orlando, FL, United States, Apr. 23-27, 2006 (2006)
16. Barthel, H.; Dreyer, M.; Gottschalk-Gaudig, T.; Litvinov, V.; Nikitina, E. Organosilicon Chemis-

- try V: From Molecules to Materials (2003), 752-766.
17. Barthel, H.; Dreyer, M.; Gottschalk-Gaudig, T.; Litvinov, V.; Nikitina, E. Macromolecular Symposia (2002), 187, 573-584
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#### Patents:

1. EP1433749     Process for the production of wettable, gentle hydrophobic and finely dispersed silica comprising a silylated surface
2. EP1473296     Silica treated with alpha-silanes and process for its manufacturing
3. DE10349082     Water based dispersions and/or emulsions of RTV-1 silicone sealants stabilized by (partial) silylated pyrogenic silica which do not cleave off VOC or contain tensides
4. DE10360464     Dispersions of silica comprising at least two different types of silica particles having different isoelectrical points
5. WO05092989     Emulsions of W/O- / O/W-typ comprising an oil phase, a water phase and sintered aggregates of pyrogenic silica at their interphase

6. WO06018144 Particles comprising a core consisting of metal oxides, metal/silicon oxides, silicon dioxide and/or silicone resins having protected isocyanate groups on the surface
7. WO06018112 pyrogenic silica stabilized emulsion comprising low amounts of electrolytes showing enhanced flowing properties
8. WO06081979 Hydroxy alkyl functional particles as filler obtainable by conversion of metal oxide, organo polysiloxane resins and/or colloidal particles with cyclic organo siloxanes in the presence of water or alcohol
9. WO06058657 Cationic silica for dispersions for the synthesis of coatings for ink jet media
10. WO06097240 Dispersions of partially hydrophobized silica for water based resins and adhesives
11. WO07012547 Sterical stabilized silica dispersed in organic or aqueous matrix comprising high filler amounts for the use in scratch resistant coatings and nano-composite adhesives
12. WO06084629 Composition for coatings comprising particles having protected isocyanato groups at the surface
13. WO08000302 Process for the production of pyrogenic silica using a combustion chamber comprising a cooling to produce silica with low amounts of impurity atoms and low amounts coarse-grained particles
14. WO07048691 Zwitterionic particles modified with ammonium-alkyl-sulfonated siloxanes and their use as filler in composite materials for the production of membranes
15. EP1845136 Alkylsilane-modified pyrogenic silica as rheological additive basic media like amine hardeners for epoxy
16. WO07113095 Core-shell particles with a substructure inducing selfcleaning properties